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Phase Purity of $NiCo_2O_4$, a Catalyst Candidate for Electrolysis of Water

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SUMMARY

$NiCo_2O_4$ is shown to be difficult to obtain as a pure phase, and may never have been so obtained. High resolution x-ray diffractometry is required for its precise characterization. Film XRD is not likely to show the asymmetry in the spinel diffraction lines, caused by poorly crystallized NiO, that is seen in diffractometer traces. The Co_3O_4 which is expected to accompany NiO as an impurity in $NiCo_2O_4$ syntheses has the same diffraction pattern as the binary oxide. Firings of the co-precipitated hydroxides at 300, 350, and 400 °C, including one in pure O_2, failed to produce single phase cobaltate. Scanning electron microscopy showed all the sintered products to range over several orders of magnitude in agglomerate/particle size. Surface areas by BET were all in the range 40 to 110 m^2/g, equivalent to particles of 200 to 100 Å diameter. The spinel diffraction line breadths were compatible with these approximate dimensions.

INTRODUCTION

The spinels, $NiCo_2O_4$ and Co_3O_4, have been widely investigated as anode catalysts for the electrolysis of alkaline water at elevated temperatures (refs. 1 to 12). Their activity and durability have been amply documented in several types of electrode structures. Phase purity of the various $NiCo_2O_4$ preparations, however, appears to be a common problem, with the presence or absence of NiO a particular uncertainty. This work was undertaken to examine the phase purity and texture/morphology of $NiCo_2O_4$ for the purpose of contributing to its characterization.

EXPERIMENTAL

The co-precipitation procedure of Betejue and Tseung (ref. 13) was used to make $NiCo_2O_4$. The first synthesis used their 400 °C 5 hr firing. Subsequent syntheses were done with a 300 °C, 10 hr, and a 350 °C, 5 hr firing. A firing was also done in 2 atm of O_2 at 300 °C for 10 hr. A commercially available specimen was also obtained and included in the measurements. The preparations were characterized by: (1) surface area (SA) by an automated BET apparatus (ref. 14) using N_2 adsorption at liquid nitrogen temperature; (2) scanning electron microscopy (SEM) for observation of morphology, texture, and particle/agglomerate size; (3) x-ray diffraction (XRD) by automatic diffractometry, Cu x-rays and a crystal monochromator after the diffraction; and (4) crystallite size as estimated from diffraction line breadth according to equation (1).

$$R_{(hkl)} = \frac{0.89\ \lambda}{(\beta_{1/2} * \cos\theta)_{hkl}} \qquad (1)$$

where

R is the radius of the (assumed) spherical crystallite

λ is the x-ray wave length, here = 1.54 A

β is the width in radians at half maximum intensity of the diffraction line above background

θ is the Bragg angle for the (hkl)

No special refinements were applied to the calculations from line breadth since an accuracy of about a factor of 2 was deemed adequate for the conditions of these experiments.

RESULTS

Table I identifies the $NiCo_2O_4$ specimens and contains some of the data. X-ray diffractometer traces were obtained with a monochromator upon the diffracted Cu K radiation. Figure 1 is the XRD pattern given by specimen 1; it shows well-resolved NiO lines and overall crystalline diffraction. Figures 2 and 3 are patterns given by specimen 2; they are marked with NiO line positions which are indicated only as asymmetry of the spinel lines. Diffraction patterns from specimens 3 to 8 were not substantially different from figure 2.

The diffraction line breadth of the spinel (220) at $2\theta = 31.05°$, from specimen number 2, is the only measurement reported here as used for calculation of crystallite size since there appeared to be no systematic relation to surface areas among the specimens. A size of R = 200 A was obtained by use of equation (1) on this (220) line. Scanning electron micrographs of specimens 1, 2, 6, and 7 are shown in figures 4 to 8 as captioned. SEM's from specimens 3 to 5 were not significantly different from 6 and 7. Specimen number 2 (fig. 5), appeared to be different from the others; the difference was resolved at high magnification (fig. 6).

DISCUSSION

Figures 2 and 3 show asymmetry in the $NiCo_2O_4$ spinel diffraction lines at $\theta = 36.8°$ and 44.7°. There is a spinel line at 38.5° which obscures the NiO line at 37.3°; however, the spinel line asymmetry indicated in figures 2 and 3 must be ascribed to NiO diffraction at $2\theta = 43.3°$. All specimens heated in this work between 300 and 400 °C to form the binary oxide yielded diffraction patterns like those of figures 2 and 3. On the other hand, figure 1, specimen number 1, shows the spinel phase well-resolved from NiO, indicated an apparently well-crystallized material probably fired »400 °C. This specimen's low SA is in accord with the XRD indications of crystallinity.

The reporting of presence or absence of NiO in $NiCo_2O_4$ has apparently been largely based on film-recorded diffraction with Cu Kα x-rays. It is here postulated that NiO impurity probably has escaped detection where it has been reported absent, because of the combination of line broadening due to small particle size, asymmetry of spinel lines due to poorly crystallized NiO, and by film darkening due to fluorescence by the transition elements caused by the incident x-ray beam (1A). Counter-diffractometry with Cu K x-rays plus crystal monochromatization should be used; an alternate is Co Kα radiation without a monochromator. In view of these observations, it is conceivable that $NiCo_2O_4$ has never been obtained as a single phase.

It is notable that Co_3O_4, which may be expected to accompany NiO, produces quite precisely the same diffraction pattern as $NiCo_2O_4$. Further, one has to contend with the range of lattice constants attributed to each spinel. Knop, et al. (ref. 15), lists 12 values for Co_3O_4 ranging from 8.05 to 8.126 A, and 4 for $NiCo_2O_4$, ranging from 8.098 to 8.128 A. Knop does show a differentiation in some relative intensities in neutron diffraction by the two substances.

SEM discloses a very wide range of particle or agglomerate size in all the specimens. Figure 6, a 2000X magnification of one of the large lumps of figure 5, shows the mass to be a porous agglomerate of much finer particles than figure 5 might suggest. Specimen 1, appearing to be well-crystallized to XRD and of low SA, is seen in figure 4 to consist of agglomerates of fines. Oxides obtained by firing co-precipitated hydroxides may exhibit morphologies like those shown here, whereas other methods may result in different morphologies. Unfortunately, the history of specimen 1 was not obtainable, In any case, it appears desirable for the fabrication of teflonated electrodes to consider the morphology of the catalyst. Agglomerates of fine particles will tend to be covered by the flow of teflon in the usual low temperature sintering applied to the teflon-catalyst mix upon its metal base.

Freeze-drying synthetic procedures have been reported to make the "best" $NiCo_2O_4$, including claim to freedom from NiO impurity (according to film XRD), yet one report (ref. 4) did find NiO in such a synthesis. In all, although excellent performance has been obtained with teflonated $NiCo_2O_4$ electrolysis anodes, it should be productive to use well-characterized catalyst.

CONCLUDING REMARKS

In general, it seems desirable to use single phase material as a catalyst. In view of good performance by $NiCo_2O_4$ electrodes of various types incorporating oxides more or less defined, it cannot be claimed that better characterization will lead to significant improvement. The contradictions in reports of performance, however, do suggest that this could happen. Control of synthesis and teflonation by use of SEM and high resolution x-ray diffractometry may be useful in this respect.

SUMMARY OF RESULTS

Scanning electron microscopy and x-ray diffractometry have shown that $NiCo_2O_4$ preparations are difficult to characterize and may never have been single phase. Firing of the co-precipitated hydroxides at 300, 350, and 400 °C resulted in $NiCo_2O_4$ with unknown amounts of NiO best detected by crystal

monochromatized x-ray diffractometry. Any accompanying Co_3O_4 cannot readily be resolved. Reports of single phase $NiCo_2O_4$ based on film recorded x-ray diffraction require re-evaluation inasmuch as amorphous NiO could have been evidenced by asymmetry of some spinel diffraction lines rather than by resolvable peaks or obscured by film darkening.

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TABLE I. - MEASUREMENTS ON $NiCo_2O_4$

[Specimens 2 to 8 had been co-precipitated as hydroxides from chlorides and fired to oxides. 3 and 4 were precipitated at 80 °C, 5 and 6 at 25 °C. 7 and 8 were taken from the hydroxide batch of 3 and fired for 10 hr in O_2; afterwards, 7 was ball-milled with Ni balls for 2 hr in isopropanol. The a_o values are averages obtained from two (hkl)'s, the (400) and the (440).]

Specimen identification			BET m^2/g	XRD observations	
Number	Firing conditions			a_o, Å	NiO identical
	T, °C	Time, hr			
1	Commercial source		7	8.106	NiO resolved.
2	400	5	40	8.109	Specimens 2
3	300	10	90	8.096	to 8 showed
4	350	5	70	8.098	asymmetry
5	300	10	95	8.080	of spinel
6	350	5	113	8.082	lines where
7	300 in O_2	5	79	8.101	NiO lines
8	300 in O_2	5	76	8.102	lie.

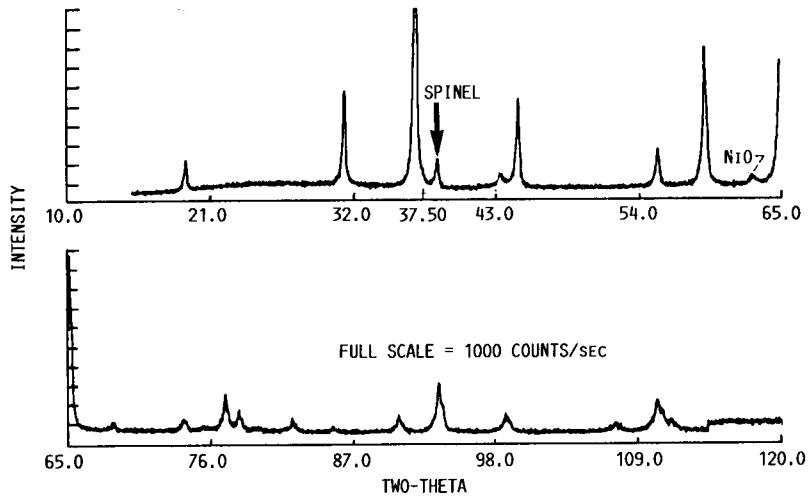

FIGURE 1. - $NiCo_2O_4$ COMMERCIAL.

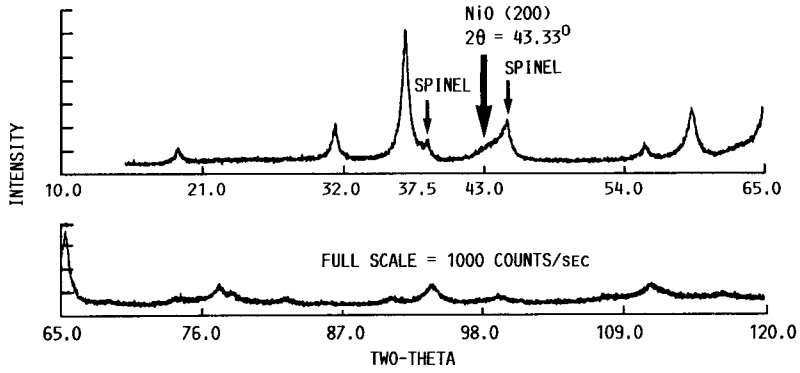

FIGURE 2. - $NiCo_2O_4$, 400 °C FIRED CO-PRECIPITATE.

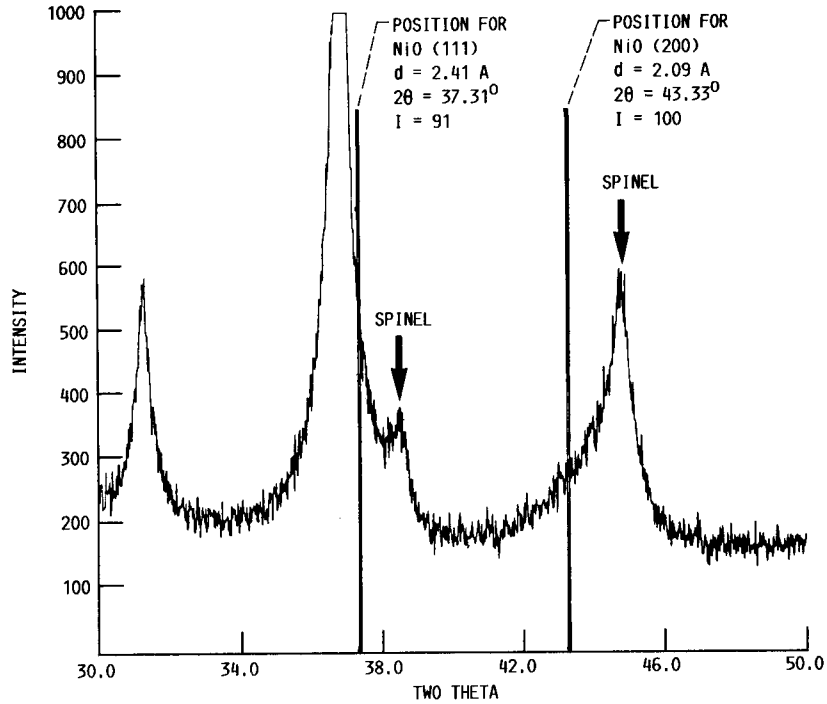

FIGURE 3. - $NiCo_2O_4$, 400 °C FIRED CO-PRECIPITATE. ENLARGED SECTION OF FIGURE 2.

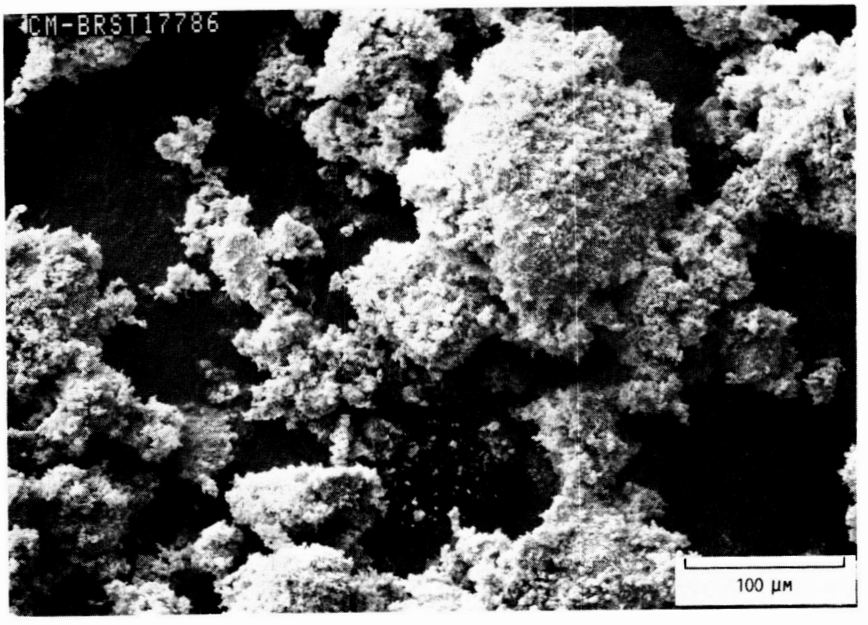

FIGURE 4. - $NiCo_2O_4$ SPECIMEN 1.

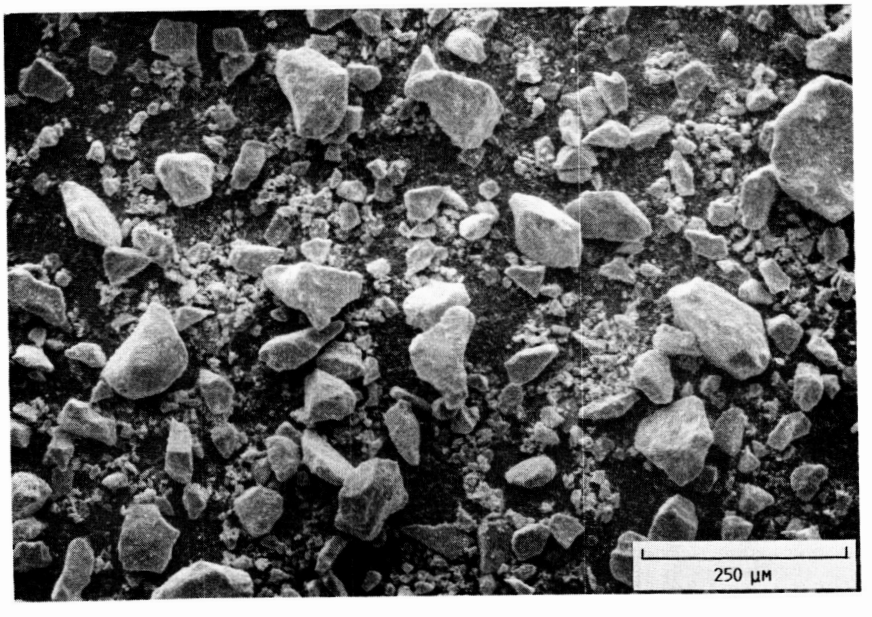

FIGURE 5. - $NiCo_2O_4$ SPECIMEN 2.

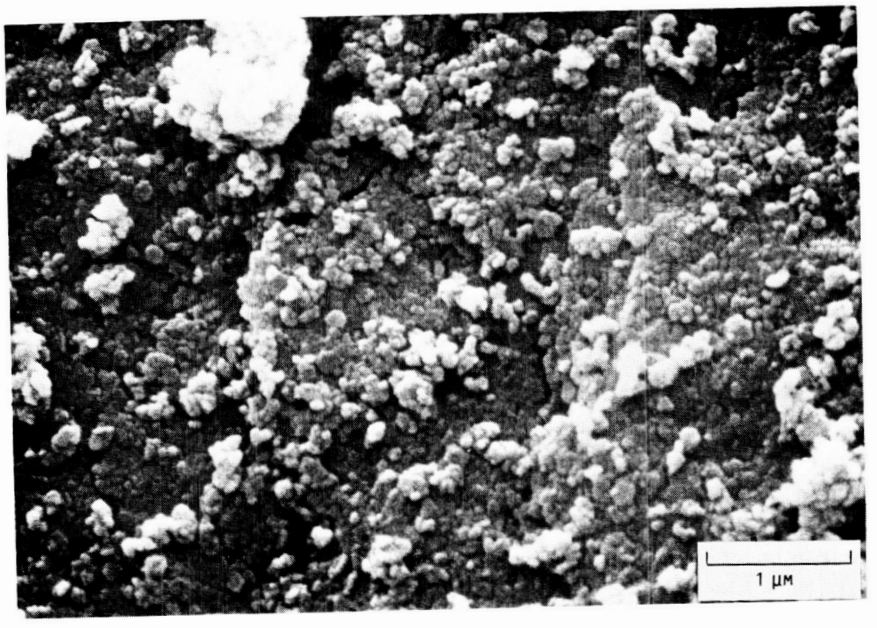

FIGURE 6. - $NiCo_2O_4$ SPECIMEN 2.

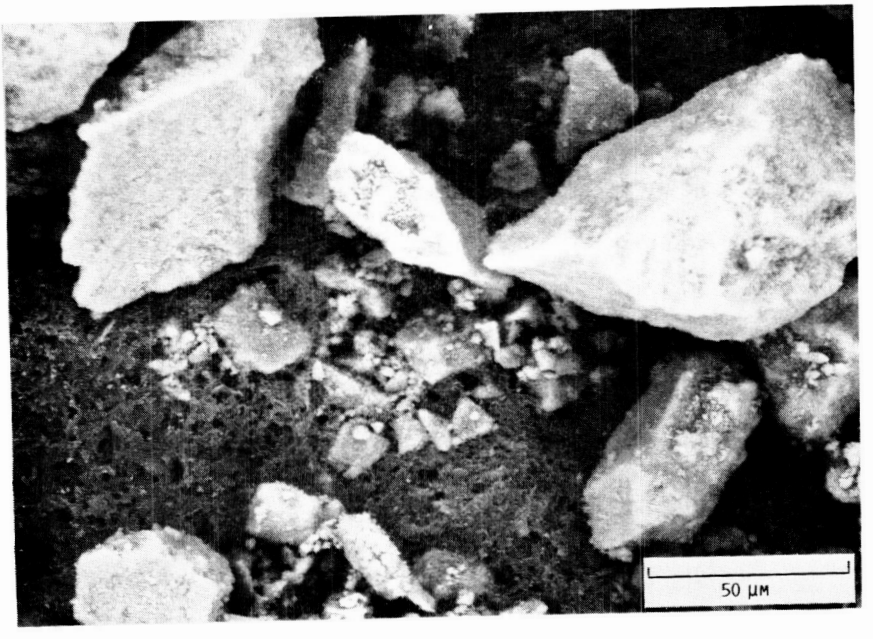

FIGURE 7. - $NiCo_2O_4$ SPECIMEN 6.

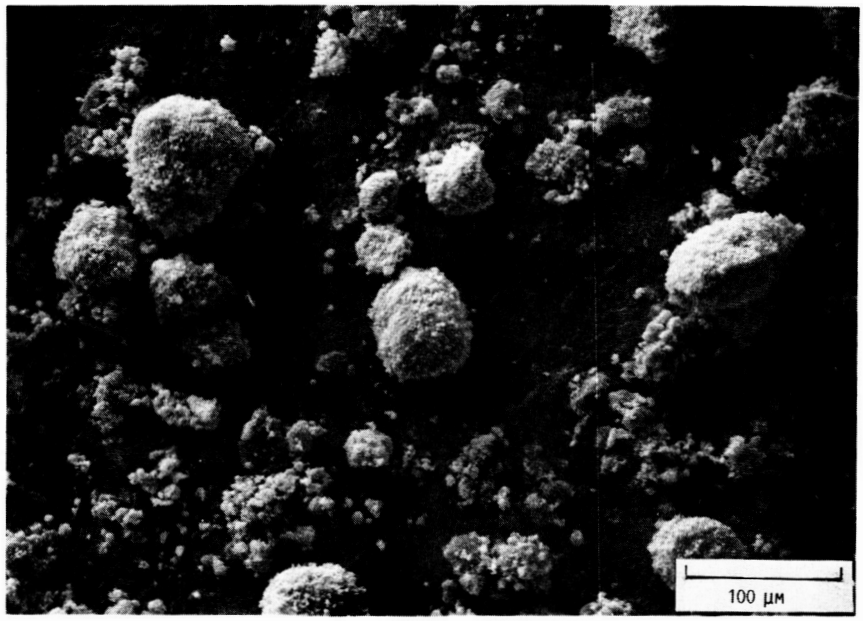

FIGURE 8. - $NiCo_2O_4$ SPECIMEN 7.

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15. *Supplementary Notes*

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16. *Abstract*

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